# Spatial Variation of Dissolution at Fracture Boundaries

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Prediction of fluid flow in fracture networks is critically important to the safe and efficient advance of geologic energy technologies including oil and gas extraction, geothermal energy systems and geologic $CO_2$ storage. Although pore-scale mineral variation can profoundly affect fracture fluid flow [1] and the mass transfer of organics, metals and salts, major knowledge gaps exist due to the lack of experimental observations of pore-scale processes at fracture boundaries. We conducted core-flooding experiments with fractured carbonate-rich caprock samples and showed that while calcite dissolution is the primary geochemical driver of alterations to fracture geometry, permeability evolves based on a complex relationship between initial fracture geometry, mineral spatial heterogeneity and variation, fluid chemistry and flow rate [2].

To investigate the underlying causes of spatial variability of dissolution and fracture geometry alteration, we developed a new flow-through cell that enables 2D x-ray imaging of mineral-specific dissolution at a fracture surface. The parallel plate design provides an idealized fracture geometry to derive the relationship between flow rate, reaction rate, and mineral spatial heterogeneity and variation. In the flow-cell, a subsample of the carbonate-rich caprock core described above was reacted with acidified brine. The extent of dissolution was spatially correlated with calcite abundance relative to less soluble dolomite and silicate minerals, which is qualitatively consistent with the core-flooding experiment. In a second set of experiments with a limestone specimen, however, the extent of dissolution was not strictly correlated with the occurence of calcite. Instead, the pattern and extent of dissolution suggested secondary causes such as calcite morphology, the presence of argillaceous minerals and other diagenetic features. These experimental results help define the combinations of brine chemistry, caprock mineralogy and flow rates with a high probability for geochemical alterations that increase fracture permeability.

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# Iron isotopes in seawater from the Southeast Pacific and North Atlantic Oceans

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Iron is an essential micronutrient for marine photosynthesis and nitrogen fixation, and low dissolved iron (dFe) concentrations limit primary production in large regions of the global ocean. Thus, understanding the sources, sinks, and internal cycling of Fe is vital to constraining its impact on the oceanic carbon cycle. Fe isotope ($\delta^{56}$Fe) measurements of dFe in seawater are a new tracer for Fe provenance and are also emerging as a useful tool for investigating Fe transformations in the open ocean.

This study presents three full-depth $\delta^{56}$Fe profiles from the Southeast Pacific Ocean (~25°S, 70-105°W) ranging from the coastal oxygen minimum zone off of Chile to the middle of the subtropical gyre near Easter Island. Upper 1000m samples demonstrated isotopically light Fe, in contrast to enriched values in the upper ocean of the North Atlantic and Southwest Pacific [1, 2]. A distal hydrothermal vent Fe signal was also detected around 2000m depth at the two offshore stations ([dFe] of 0.86 and 1.45 nmol/kg) and corresponded to an enriched $\delta^{56}$Fe signature of +0.5‰ at both stations.

We also present $\delta^{56}$Fe values of size fractionated dFe at two stations sampled on the U.S. GEOTRACES cruise in the North Atlantic Ocean: one near Bermuda and one near the Cape Verde Islands. Surface dFe (<0.2 $\mu$m) $\delta^{56}$Fe values were near +0.5‰ at both stations, while the soluble Fe (<10 kDa) portion of the dFe phase was significantly enriched in excess of +1.0‰. Subsurface soluble Fe was the same or slightly depleted compared to dFe. This demonstrates that, at least in the surface ocean, soluble and colloidal Fe are cycling independently.

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[2] Radic *et al* (2011) *Earth Planet Sc Lett* **306**, 1-10.

DOI:10.1180/minmag.2013.077.5.6